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(54) Title of the Invention: Process for the Production of Pigment-coated Paper

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**SPECIFICATION****1. Title of the Invention**

Process for the Production of Pigment-coated Paper

**2. Claims**

(1) A process for the production of pigment-coated paper characterized in that a binder is added to a pigment slurry in which the proportion of ground calcium carbonate, consisting of a component having an average particle size of from 0.3 to less than 1.5  $\mu$ m and a component having an average particle size of 1.5-5  $\mu$ m, and kaolin is 75:25-25:75, and a coating, the solids fraction concentration of which has been adjusted to 63-75%, is applied to the surface of a paper by a blade coater, and then dried.

(2) The process for the production of pigment-coated paper of Claim 1 wherein the mixture ratio of ground calcium [sic] having an average particle size of from 0.3 to less than 1.5  $\mu\text{m}$  and that having an average particle size of 1.5-5  $\mu\text{m}$  is 90:10-50:50.

(3) The process for the production of pigment-coated paper of Claims 1 or 2 wherein the binder is a synthetic latex [sic] binder.

(4) The process for the production of pigment-coated paper of Claims 1 or 2 wherein the binder is a mixture of a synthetic latex [sic] binder and a water-soluble binder.

(5) The process for the production of pigment-coated paper of any of Claims 1 to 4 wherein the solids fraction concentration of the coating is 63-75%.

(6) The process for the production of pigment-coated paper of any of Claims 1 to 5 wherein the coating viscosity is 70 centipoise or less by Hercules viscometer at a shear speed of  $9.2 \times 10^4 \text{sec}^{-1}$ .

### 3. Detailed Description of the Invention

The present invention relates to a process for the production of pigment-coated paper. In particular, it relates to a process that provides stable operational efficiency, lowers the drying energy [sic], and produces high-quality pigment-coated paper by using a coating that contains a high solids fraction containing a large amount of inexpensive ground calcium carbonate by blade coater.

The properties of coated paper demanded by the marketplace are diversifying even as increasing demands are being placed on raising the coating speed in the production of pigment-coated paper. Blade coating is particularly advantageous for forming a smooth, dense coating layer by using a coating having a high solids fraction. However, the properties of the coating used become important for assuring stable operational efficiency and good product quality because the base paper is coated while applying high shear stress to the coating by the tip of the blade in this case.

Calcium carbonate has often been used in the past in combination with other pigments such as kaolin to improve the whiteness of the coated paper, ink dryability, and the like in the production of pigment-coated paper. Calcium carbonate is broadly classified as two types: one of which is a natural product (ground calcium carbonate) obtained simply by mechanically crushing

limestone and the other of which is a precipitated product (precipitated calcium carbonate) produced by a chemical reaction. Each product comes in various types depending on the particle size and shape; and each type has different functions.

The percentage of calcium carbonate in high-gloss coated paper is generally 20 wt% or less. The reason for this is that more than 20% decreases the gloss or surface strength of the coated paper. Recent research has reported obtaining high-gloss coated paper by raising the solids fraction of the coating and increasing the percentage of calcium carbonate, but the calcium carbonate used is limited to that having an average particle size of 1  $\mu\text{m}$  or less and containing 85 wt% or more having a particle size of 2  $\mu\text{m}$  or less. According to the results of studies conducted by the present inventors, combining a large amount of ground calcium carbonate of such a particle size increases the viscosity of the coating and lowers the surface strength of the coated paper.

However, the present inventors discovered that such problems are resolved when calcium carbonate of a large particle size that had been deemed unsuitable for high-gloss coated paper in the past is used. Nonetheless, the gloss of the coated paper declines markedly when calcium carbonate of a large particle size is used, as was commonly thought up to this point.

As a result of studying the use of a large amount of ground calcium carbonate and production processes capable of improving the gloss and surface strength of the coated paper, they discovered that:

- (1) A coating having good fluidity must be applied and evened smoothly by the blade of the blade coater.
- (2) A coating having as high a solids fraction as possible should be applied to control movement of the pigment particles associated with changes in the water content during drying.
- (3) It is difficult to obtain a smooth coating layer surface by blade from coarse pigment particles alone; fine pigment particles must be admixed.

Calcium carbonate is suitable for making a coating having a high solids fraction because it has a hydrophobic function, but mixing coarse particles and fine particles is a requisite condition for satisfying the above three demands.

The average particle size of the ground calcium carbonate in the present invention was measured by the Andreasen pincet [sic] method based on JIS M 8016 (test methods for clay for papermaking).

Concretely speaking, they discovered that coated paper having high gloss and high printing strength can be obtained if the pigment consists mainly of ground calcium carbonate and kaolin in a ratio 75:25-25:75, the average particle size of the ground calcium carbonate therein is a 90:10-50:50 mixture of a component of from 0.3 to less than 1.5  $\mu\text{m}$  and a component of 1.5-5  $\mu\text{m}$ , preferably 2-4  $\mu\text{m}$ , dispersed in water by a dispersant, and the coating having good fluidity is applied by the blade tip and dried after adding mainly a synthetic latex binder and a water-soluble binder and adjusting the solids fraction to 63-75%, preferably 65-72%, by stirring, and thereby achieved the present invention.

As a result of studies that varied the added proportion of synthetic latex binder and water-soluble binder while maintaining the surface strength of the coated paper, the present inventors also discovered that processing by a blade coater becomes possible even when the pigment solids fraction is increased due to the conspicuous decline in the viscosity of the coating and that the gloss of the coated paper improves greatly when a synthetic latex binder is used alone without adding a water-soluble binder.

The pigment in the present invention is mainly ground calcium carbonate and kaolin, but titanium dioxide, aluminum hydroxide, satin white, plastic pigment, and the like may also be combined as is appropriate.

Starch and modified forms thereof, casein, soybean protein, cellulose derivatives, and other such water-soluble binders and styrene-butadiene-based latexes, methacrylate-butadiene-based latexes, acrylic-based latexes, ethylene-vinyl acetate-based latexes, and other such synthetic latexes are used individually or in combination as the binder used in the present invention.

Dispersants, fluidity-adjusting agents, defoaming agents, dyes, lubricants, waterproofing agents, humectants, and other such auxiliaries commonly used in coatings can also be used.

The following reasons are believed to be why a coated paper having high gloss and high printing strength is obtained under the above conditions.

(1) When coarse ground calcium carbonate having an average particle size of 1.5-5  $\mu\text{m}$  and fine ground calcium carbonate of from 0.3 to less than 1.5  $\mu\text{m}$  are used in mixture with kaolin, the spaces between the pigment particles of the coarse ground calcium carbonate are filled appropriately by the fine ground calcium carbonate and kaolin, compensating for the decrease in the gloss of the coated paper caused by the use of coarse ground calcium carbonate and the decline in the surface strength of the coated paper caused by the use of fine ground calcium carbonate.

(2) Combining a larger amount (75-25 wt%) of calcium carbonate than kaolin and combining coarse and fine calcium carbonate lowers the coating viscosity, makes the fluidity at the tip of the blade good even when the coating solids fraction is raised, and allows the coating layer to be evened smoothly because the hydrophobic function of the calcium carbonate interferes with the aggregating effect between the pigments.

The fluidity of the coating at the blade tip can be evaluated by measuring the viscosity under high shear speed. The present inventors' experience shows that good blade coating becomes difficult when the viscosity by Hercules viscometer at a shear speed of  $9.2 \times 10^4 \text{sec}^{-1}$  exceeds 70 centipoise.

(3) The coating solids fraction for a blade coater is generally 55-62 wt%, but the amount of water to be removed in the drying step after coating becomes very small and it is easy to keep the coating layer properly filled with pigment when the concentration is 63-75 wt%.

Points that characterize the present invention will be further clarified below through working examples.

## Working Examples 1-9

Fine ground calcium carbonate having an average particle size of 0.5  $\mu\text{m}$ , 0.7  $\mu\text{m}$ , and 1.3  $\mu\text{m}$ , coarse ground calcium carbonate having an average particle size of 2.4  $\mu\text{m}$  and 3.8  $\mu\text{m}$ , and kaolin having an average particle size of 0.6  $\mu\text{m}$  and 0.8  $\mu\text{m}$  were used, and their proportions were varied in each working example. The pigment ratios are shown in the table together with the results.

The respective mixed pigments were dispersed in water by 0.3 part by weight of polyacrylic-based dispersant (made by Toagosei Chemical Co., trade name Alon T-40), and a clay slurry having a solids fraction of 73 wt% was prepared. Ten parts by weight of styrene-butadiene-based latex (made by Japan Synthetic Rubber, trade name JSR 0692) were added, followed by addition of acidified starch (made by Shikishima Starch Co., trade name Marmaid 210) and mixing by stirring. A coating having a final solids fraction of 64-68 wt% was obtained.

This coating was measured by B type and Hercules viscometers by the following method, and the results are shown in the table.

Paper having a basis weight of 60 g/m<sup>2</sup> consisting of 100% LBKP coated with starch by a size press was coated using this coating so that the amount applied would be 14 g/m<sup>2</sup> by dry weight on one side and dried. After conditioning, coated paper was produced by supercalendering at a temperature of 50°C and linear pressure of 100 kg/cm.

The gloss and surface strength of the coated paper were measured by the following methods, and the results are shown in the table.

1) B type viscosity: Value of a B type viscometer (Brookfield viscometer, model BM, made by Tokyo Keiki Kogyo), 60 rpm, 30°C

2) Hercules viscosity: Value of a Hercules viscometer, 4400 rpm, 30°C, shear speed  $9.2 \times 10^4 \text{sec}^{-1}$

3) Gloss: 75°-75° mirror surface gloss (made by Murakami Color Co.)

#### 4) Surface strength: IGT tester

A product of the trade name Ultrawhite 90 (made by Engelhard MC Co., USA, premium No. 1 grade kaolin) was used as the kaolin having an average particle size of 0.6  $\mu\text{m}$ . A product of the trade name MT (made by the above company, standard No. 2 grade kaolin) was used as the kaolin having an average particle size of 0.8  $\mu\text{m}$ .

#### Comparative Examples 1-6

Fine ground calcium carbonate having an average particle size of 0.5  $\mu\text{m}$ , 0.7  $\mu\text{m}$ , and 1.3  $\mu\text{m}$ , coarse ground calcium carbonate having an average particle size of 2.4  $\mu\text{m}$  and 3.8  $\mu\text{m}$ , and kaolin having an average particle size of 0.6  $\mu\text{m}$  and 0.8  $\mu\text{m}$  were used as the pigments, and their proportions were varied in each comparative example. The pigment ratios are shown in the table.

Each mixed pigment was dispersed in water by 0.3 part by weight of a polyacrylic-based dispersant, and clay slurries of 73 wt% were prepared in Comparative Examples 1-4 and of 71 wt% were prepared in Comparative Examples 5 and 6. Ten parts by weight of styrene-butadiene-based latex and 2.5 parts by weight of acidified starch were added, and coatings having final solids fractions of 61-67 wt% were obtained by stirring and mixing.

The method was otherwise exactly the same as in Working Examples 1-9, and the results are shown in the table.

In Comparative Example 5, the coating quantity was too high due to the high Hercules viscosity even when the blade coater coating conditions were changed, and the coating quantity could not be kept to 14  $\text{g}/\text{m}^2$ .

#### Working Examples 10-12

Fine ground calcium carbonate having an average particle size of 0.7  $\mu\text{m}$ , fine [sic] ground calcium carbonate of 2.4  $\mu\text{m}$ , and kaolin of 0.6  $\mu\text{m}$  were used as pigments. Their ratios were varied in each working example and are shown in the table.

Each mixed pigment was dispersed in water by 0.3 part by weight of a polyacrylic-based dispersant, and clay slurries having a solids fraction of 73 wt% were prepared. Eleven parts by weight of styrene-butadiene-based latex alone were added to these as a binder, and coatings having final solids fractions of 69-70.5 wt% were obtained by stirring and mixing.

The method was otherwise exactly the same as in Working Examples 1-9, and the results are shown in the table.



	Pigment composition (parts)							Binder composition (parts)		Coating solids fraction (%)	Coating viscosity (cps)		Coated paper quality	
	Fine ground calcium carbonate			Coarse ground calcium carbonate		Kaolin		Styrene-butadiene latex	Acidified starch		B type	Hercules	Gloss (%)	IGT pick (cm/sec)
	0.5 μm	0.7 μm	1.3 μm	2.4 μm	3.8 μm	0.6 μm	0.8 μm							
Working example 1	40				10	50		10	2.5	67	2200	54	67	160
Working example 2		40			10	50		10	2.5	67	2100	50	66	170
Working example 3			40		10	50		10	2.5	67	1620	48	62	180
Working example 4		40				50		10	2.5	67	1800	50	62	190
Working example 5		50			10	40		10	2.5	68	2300	55	64	190
Working example 6		20			10	70		10	2.5	65	1000	50	62	170
Working example 7			20		10	70		10	2.5	65	900	50	64	160
Working example 8		20			10		70	10	2.5	65	1100	52	63	160
Working example 9		20			20	60		10	2.5	66	1300	50	62	170
Comparative example 1	50					50		10	2.5	67	3500	57	66	120
Comparative example 2		50				50		10	2.5	67	2500	55	65	130
Comparative example 3			50			50		10	2.5	67	2000	53	65	135
Comparative example 4				50		50		10	2.5	67	920	48	47	210
Comparative example 5		20				80		10	2.5	67	1800	80	—	—
Comparative example 6		20				80		10	2.5	62	600	48	65	120
Working example 10		40			10	50		11	0	69	1250	50	73	150
Working example 11		50			10	40		11	0	70	1500	55	70	170
Working example 12		60			10	30		11	0	70.5	2000	55	69	180

## Procedural Amendment

July 14, 1980

To the Director of the Patent Agency, Takao Kawahara

## 1. Disclosure of case

Patent Application 55-62738

## 2. Title of the invention

Process for the production of pigment-coated paper.

## 3. Person submitting amendment

Relationship to case: Applicant

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## 5. Voluntary amendment

(Submitted on same date as request for examination)

## 6. Object of amendment

Claims and Detailed Description of the Invention

## 7. Content of amendment

The following parts of the specification are amended.

(1) The Claims on p. 1 line 4 to p. 2 line 11 are amended on a separate sheet.

(2) Line 4 from the bottom of p. 2

"Of drying" is amended to read "required for drying."

(3) Bottom line, p. 5

"Andreasen pincet" is amended to read "Andreasen pipette."

(4) Line 12, p. 7

"Methacrylate" is amended to read "methyl methacrylate."

(5) Line 12, p. 11

"Trade name MT" is amended to read "trade name HT."

## 2. Claims

(1) A process for the production of pigment-coated paper characterized in that a binder is added to a pigment slurry in which the proportion of ground calcium carbonate, consisting of a component having an average particle size of from 0.3 to less than 1.5  $\mu\text{m}$  and a component having an average particle size of 1.5-5  $\mu\text{m}$ , and kaolin is 75:25-25:75, and a coating, the solids fraction concentration of which has been adjusted to 63-75%, is applied to the surface of a paper by a blade coater, and then dried.

(2) The process for the production of pigment-coated paper of Claim 1 wherein the mixture ratio of ground calcium carbonate having an average particle size of from 0.3 to less than 1.5  $\mu\text{m}$  and that having an average particle size of 1.5-5  $\mu\text{m}$  is 90:10-50:50.

(3) The process for the production of pigment-coated paper of Claims 1 or 2 wherein the binder is a synthetic latex binder.

(4) The process for the production of pigment-coated paper of Claims 1 or 2 wherein the binder is a mixture of a synthetic latex binder and a water-soluble binder.

(5) The process for the production of pigment-coated paper of any of Claims 1 to 4 wherein the solids fraction concentration of the coating is 63-75%.

(6) The process for the production of pigment-coated paper of any of Claims 1 to 5 wherein the coating viscosity is 70 centipoise or less by Hercules viscometer at a shear speed of  $9.2 \times 10^4 \text{sec}^{-1}$ .

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